

GF-AASによるフライアッシュ中ヒ素濃の直接定量

Direct Determination of Arsenic Concentration in Coal Fly Ash by GF-AAS

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Abstract

The discharge of fly ash from coal combustion processes has become a matter of concern in the world over last few decades. Arsenic as one of the most highly toxic chemical which is contained in coal fly ash gives negative impacts on human health and global environment. The graphite furnace atomic absorption spectroscopy (GF-AAS) method has been proposed for direct determination of element in solid sample since its appearance as a good alternative to wet methods of analysis in many matrices. Here, we examine the use of GF-AAS for total arsenic determination in coal fly ash from distinct coal mines in Indonesia. Our Direct Analysis of 21 selected coal fly ashes was not always free of spectral matrix interference (since the characteristic of arsenic is the large difference in the volatility of its compounds, while the oxides are highly volatile, other compounds are very stable, these properties may lead to analyte loss during pyrolysis and in the first stage of atomization), but the spectroscopic technique and the using of matrix modifier gave a good result for total arsenic determination. The calculation of mass balance showed that this method is feasible enough as one of several methods in determination of arsenic.

1. 緒言

Major fractions of coal fly ash generated from pulverized coal combustion processes have been used as fill materials to reclaim land from the sea. Coal fly ash contains hazardous toxic elements such as arsenic, and often contains elevated concentrations of the toxic elements. An ash storage area is usually holding seawater and rainwater (called excess water), therefore some elements including arsenic in the fly ash are leach out the excess water. If arsenic concentration in the excess water exceeds the environmental limit (0.1 mg/L in Japan), the excess water can not be drained to the sea. This is a serious situation, because ash storage has to discontinue.

In this concern, it is important to analyze rapidly arsenic in the fly ashes for various coal types. Direct analysis of solid samples using graphite furnace atomic absorption spectroscopy (SS-GFAAS) method has been proposed for direct determination of elements in solid sample since its appearance as a good alternative to the wet methods of analysis that involve sample dissolution steps which are time consuming⁽¹⁾. The main advantages of the technique are its low detection limits, the minimum sample

manipulation, its relative simplicity and the short time required to obtain a result⁽²⁾. The drawbacks of SS-GFAAS are associated with increasing interferences, difficulties in calibration and sample inhomogeneity at the micro levels required⁽³⁾.

Coal as a kind of fossil fuel which cheaper than oil, is mainly used as fuel for thermal power generation in Japan, China, Indonesia, India and Vietnam. The coal combustion process will generate coal ash (fly ash) and discharge hazardous trace elements such as arsenic, lead, mercury, and chromium. This discharging has become as matter of concern in the world over last few decades. For the sake of environmental conservation in Asia, many studies of mercury⁽⁴⁾, lead⁽⁵⁾ and chromium⁽⁶⁾ analysis have been conducted in recent years, and the analytical methods had been established. Associated with many interferences in analyzing arsenic due to the volatility system and compounds of arsenic element, the analytical method has not been established yet.

Arsenic (As) as one of the most highly toxic chemical which is contained in coal fly ash, is a semi-metal element, commonly found as arsenide and in arsenate compounds, odorless, tasteless, and notoriously poisonous metalloid and dangerous for the environment with many allotropic

forms. According to EU regulation (98/83/EC) and a provisional guideline of WHO, the critical concentration of Arsenic on human health effect (in drinking water) is 10 µg/L. Arsenic in aquatic ecosystems occurs in distinct oxidation states depending on potential redox values. Its solubility in water depends on oxygen concentration, the presence of sulfur and ferric hydroxides, and biomethylation processes⁽⁷⁾. Arsenic is easily accumulated in sediments by chemical and physical binding or by adsorption onto organic and inorganic particles. The present paper focuses on the use of SS-GFAAS as a technique for validation purposes as in the case of arsenic determination in coal fly ash.

Total As content in coal can be a good indicator of contamination and its determination can be carried out directly on the solid phase by means of spectroscopic techniques, such as X-ray fluorescence (XRF) or ICP Atomic Emission Spectroscopy (ICP-AES). The further target of this paper is to develop analytical methods for chemical form of arsenic toxicity and to reveal the amount of arsenic from fly ash emitted to the environment through studying the leaching process of total arsenic in coal fly ash.

2. 実験装置および実験方法

A single-beam atomic absorption spectrometer (model novAA400, Analytik Jena) was used for the measurements. This instrument is equipped with a monochromator Czerny-turner-design mounting with a plain holographic grating system 1800 lines/mm which covers a wavelength range from 185 to 900 nm. The spectrometer combines a new transverse-heated graphite furnace atomizer with high-aperture optics and fast background compensation based on an optimised deuterium hollow cathode lamp. The optic system provides efficient background compensation by means of transillumination of equal absorption volumes for both, measurement and correction. Solid and liquid sample introduction modes are possible with a quick change and realignment of the system. For solid samples, we used a Sartorius microbalance and pyrolytically-coated platform boats were used as sample carriers.

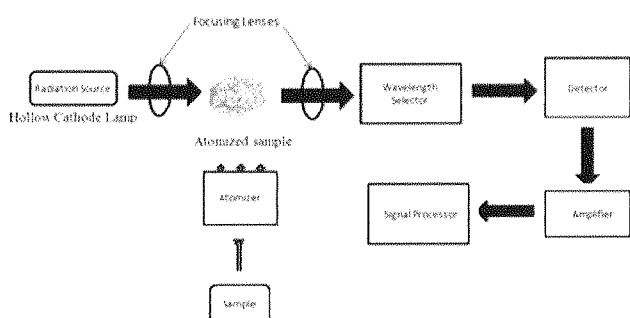


Fig.1 Schematic of an atomic absorption experiment

Standard Sample for Calibration, As were prepared from

certified reference materials (CRM) NIST 1633b, (As conc. = 136.2±2.6 mg/kg). Solvent for CRM NIST 1633b is α-Alumina (α- Al₂O₃) powder. Matrix modifier was prepared from Palladium (Pd(NO₃)₂) 40 %. Solvent for Palladium is HNO₃ 40% and distilled water. Twenty one samples of coal fly ash were imported from distinct Indonesian coal mines (Kalimantan Island, Indonesia).

For determining the arsenic concentration in coal fly ash was conducted by atomic absorption spectrometer (novAA 400, Analytik Jena) in the wavelength 193.7 nm, slit width and lamp current of Hollow Cathode Lamp are 1.2 nm and 6.0 mA respectively. The integration time was 6.0 s. The steps of the furnace program were run as described in the table below:

Table 1 Spectrograph settings and optimized furnace program of As

Spectrometer							
Line	193.7 nm	Slit	1.2 nm				
Lamp type	HCL	Lamp current	6.0 mA				
D2HCL curr.	15.5 mA	Integr. time	6.0 s				
Furnace							
No	Type	Temp [°C]	Rate [°C/s]	Hold [s]	Time [s]	Gas	
						Inert	Add g
1	preheating	70	1	60	114	Min	Stop
2	Drying	105	10	30	33.5	Min	Stop
3	Drying	120	10	20	21.5	Min	Stop
4	Ashing	600	100	20	24.8	Max	Stop
5	Ashing	1200	100	20	26	Middl	Stop
6	Ashing	500	100	50	57	Max	Stop
7	AZ*	500	0	6	6	Middl	Stop
8	Atomize	2150	500	7	10.3	Middl	Stop
9	Cleanout	2800	1000	15	15.5	Max	Stop

3. 実験結果

(3.1) Optimization of instrumental parameters

The second most sensitive wavelength for As was selected because of the relatively high contents of arsenic element in coal fly ash and in the CRM (certified reference material).

For the short wavelength (193.7 nm), the sample was atomized all (perfectly (100%), known from the instrument sensitivity) but the effect is high interferences, while for the long wavelength (197.2 nm), the sample was atomized partly (53%) and the effect is low interferences. To get the optimum result, the authors choose the second wavelength, in order to get the relatively high contents in coal fly ash. To minimize the high interferences (i.e. another element in coal) in the second wavelength, the measurement of background (another element effect) was used and appeared on the data output. When the reader repeat the same experiment, this selection of wavelength not because

to be done for particular coal, but it is more focus to be applied in general case.

Two previous drying steps were done in order to achieve a correct dryness for the solvent of matrix modifier (distilled water) without splatter. Optimization of furnace program was focused on ashing and atomization steps. Dry ashing procedures use a high temperature between 500-1200°C, water and other volatile material are vaporized and organic substances are burned in the presence of the oxygen in air to CO₂, H₂O, and N₂⁽⁸⁾. For each step hold time and the gas flow of Argon were studied. For atomizing, the temperature used was 2150°C, the criteria considered for establishing the parameters was a low background signal that did not disturb the measurement and a good sensitivity for the signal peak of the analyte.

(3.2) Establishment of quality parameters

Calibration Curve was constructed by running a series of calibration standards through the instrument. The instrument recorded the absorption generated by a given concentration. By plotting the absorption versus the concentrations of the standards, a calibration curve could be plotted to determine the concentration sample. This Calibration Curve was constructed directly and the concentrations of samples obtained automatically on output device by the data system. The Variety of concentration of arsenic are 136.2 (mg/kg), 68.1 (mg/kg), 34.05 (mg/kg), 17.03 (mg/kg). The coefficient calibration of regression is 0.9350.

The results obtained for twenty one samples (sample EP1 E to EP1 K, sample EP2 E to EP2 K, EP3 E to EP3 K) respectively could be shown in the Table 2.

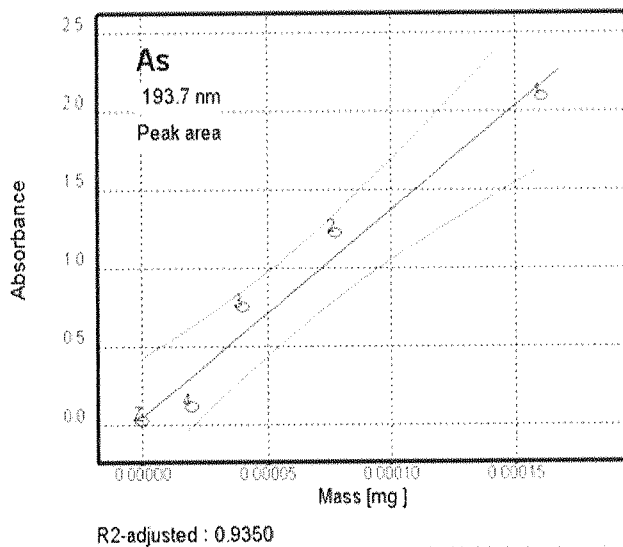


Fig. 2 Calibration Curve (black line) for direct solid sample determination of arsenic by GF-AAS. Green lines: limits of scattered data.

Table 2 The Concentration of Arsenic (ppm) in samples

Sample	EP1 Conc.	EP2 Conc.	EP3 Conc.
E	9.339	26.27	39.12
F	10.55	12.13	27.03
G	4.628	21.50	31.84
H	42.94	54.42	57.85
I	40.85	42.78	45.05
J	18.57	27.82	41.02
K	10.96	15.97	13.21

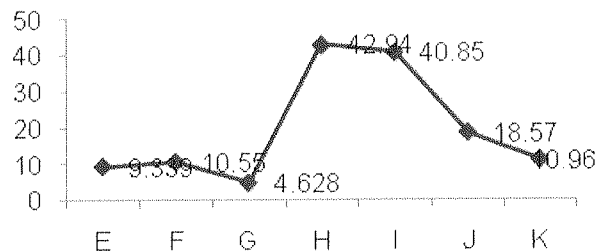


Fig. 3 The Concentration of Arsenic (ppm) in samples EP1 E to Ep1 K.

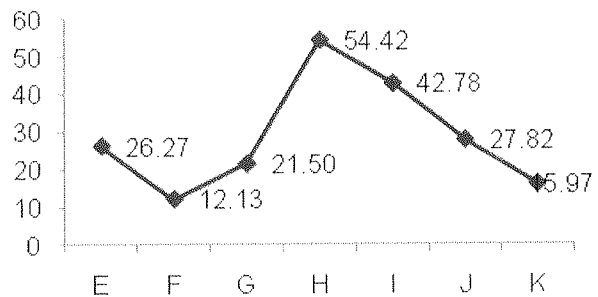


Fig. 4 The Concentration of Arsenic (ppm) in samples EP2 E to Ep2 K.

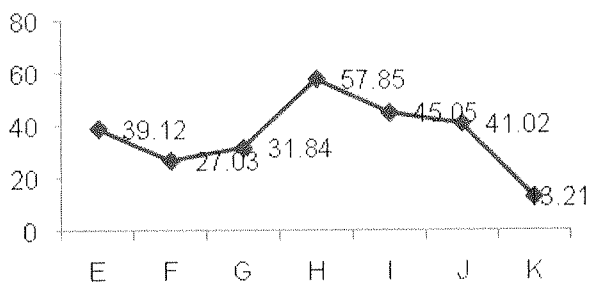


Fig. 5 The Concentration of Arsenic (ppm) in samples EP3 E to Ep3 K.

Table. 3 Mass balance data for As

Sample	Mass balance (%) of As
E	95.8
F	255.4
G	170
H	137.1
I	126.1
J	64.4
K	145.8

Validation Method through calculating Mass Balance,

$$As' = (As_o / ash) \times 100 \% \quad (1)$$

4. 結言

Graphite furnace atomic absorption spectroscopy (GF-AAS) can be used for direct solid sample to determine the concentration of arsenic in coal fly ash. The calculation of mass balance as a validation for this method show that this method is feasible enough as one of several methods in analyzing arsenic in coal fly ash.

使用記号

As' = Mass balance of arsenic

As_o = Arsenic conc. (ppm) in raw coal

(the data for the concentration of As in raw coal had been available, from the previous research)

ash = % raw coal ash content, db.

(the data which the authors got through this research about direct determination by GF AAS)

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